1,174,046

PATENT SPECIFICATION

NO DRAWINGS

1,174,046

Date of Application and filing Complete Specification: 7 Dec., 1966.

No. 54772/66.

Application made in Japan (No. 75528) on 8 Dec., 1965.

Complete Specification Published: 10 Dec., 1969.

Index at acceptance: —C3 P(4A, 4C2, 4C7, 4C13B, 4C20C, 4C20D1, 4C20D3, 4D1B, 4D1D, 4D8, 4K6, 4K8, 4K9, 4K10, 8A, 8C2, 8C7, 8C13B, 8C20C, 8C20D1, 8C20D3, 8D1A, 8D1B, 8D2A, 8D2B2, 8D4, 8D8, 8K4, 8K6, 8K8, 8K9, 8K10, 9A, 9C2, 9C7, 9C13B, 9C20C, 9C20D1, 9C20D3, 9D1A1, 9D1A3, 9D1B1, 9D1B3, 9D1X, 9D2, 9D8, 9K4, 9K6, 9K8, 9K9, 9K10, 10A, 10C2, 10C7, 10C13B, 10C20C, 10C20D1, 10C20D3, 10D1A, 10D2A, 10D8, 10K4, 10K6, 10K8, 10K9, 10K10); A2 D(2P, 3C)

International Classification:—C 08 f 37/00

COMPLETE SPECIFICATION

Synthetic Resin Film

We, KUREHA KAGAKU KOGYO KABUSHIKI KAISHA, a joint-stock company of Japan, located at 8,1-Chome, Nihonbashi Hirodome-Cho, Chuo-Ku, Tokyo-To, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to synthetic resin films which may be used as casings or wrappings for such animal food as minced fish meat "hams" and sausages for domestic animals which casings or wrappings adhere completely and intimately to the encased products. In particular, the invention relates to a new and improved casing film material produced from vinylidene chloride resins.

With the development of vinylidene chloride resin films, the periods for which hashed or minced meat food products, such as so-called "hams" (kneaded or compressed minced meat products) and sausages, may be preserved, have been greatly lengthened whereby the marketability of these products has been extended.

However, differences in the degree of close adherence between the vinylidene chloride resin casing and the encased contents are caused by very slight variations in such factors as the kinds of the meats used as basic material, their freshness, and the proportions of fats and oils. Unless exact adherence is attained, liquid juices separate from within the food meats and reduce the commercial value of the products. At the same time, the resistance of the product to contamination by microorganisms is lowered, and so the product readily deteriorates. It has thus been necessary to develop films which readily adhere to meat products under all practical conditions for use in the meat processing industry.

One factor which considerably influences the close adherence between a minced meat product, i.e. a high protein food product, and the casing film is that caused by variation in the water-retaining property of the film following degeneration of a protein. When the water-retaining property weakens, the bound water of the protein is exuded and appears between the casing film and the surface of the meat product and is considered to be the principal cause of reduction of adherence therebetween.

Therefore, in order to obtain a good degree of adherence between the film and the meat product, the only method hitherto known has been to provide the surface of the film with an agent or function which increases the water-retaining property of proteins. Among substances which increase the water-retaining property of the films with respect to proteins, are phosphates, and anionic surface active agents.

When phosphates are applied to the surface of a resin film, they are easily removed from the surface since they are inorganic substances, and it is difficult to utilize them effectively. When phosphates are blended with the film material, they cause "fish-eyes" and pinholes within the film because of the

[*Price 4s. 6d.*]

incompatibility between phosphates and the film. The film thus becomes unsatisfactory for packaging purposes.

On the other hand, while anionic surface acitive agents may be easily applied to the surface of a film and lead to improved adherence, the use of agents of this type as additives to food products is prohibited by law in the United Kingdom (see preservatives in Food Regulations 1962, No. 1532). Thus, the use of both of the abovementtioned types of agents is unsatisfactory.

The present invention however provides a casing film material having good adherence with respect to kneaded meat food products, which casing material comprises a terpolymer resin prepared by the polymerisation together of vinylidene chloride, vinyl chloride, and a compound copolymerizable therewith, which compound is an amide of an unsaturated monocarboxylic acid or dicarboxylic acid having at least one amide group in the molecule, a half ester of an unsaturated dicarboxylic acid having one free carboxyl group, or an unsaturated alcoholic compound having within its molecule at least one hydroxyl group, the compound polymerizable with the vinylidene chloride and the vinyl chloride being present in the casing film material in an amount of from 0.01 to 5 per cent by weight, based on the total monomer components in the vinylidene chloride containing resin.

Examples of acids whose monoamides or diamides can be used according to the invention are acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, and aconitic acid. Examples of suitable half esters are the monoalkyl esters of maleic acid, fumaric acid, itaconic acid, and aconitic acid having 1 to 8 carbon atoms in the alkyl group.

Examples of the above-mentioned unsaturated alcoholic compounds are allyl alcohol, methallyl alcohol, and hydroxyalkyl esters (from 2 to 6 carbon atoms in the alkyl group) of the above-mentioned unsaturated organic acids. Examples of these hydroxyalkyl esters are hydroxyethyl acrylate, hydroxymethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, hydroxybutyl methacrylate, mono- or dihydroxyethyl maleate, mono- or dihydroxypropyl maleate, mono- or dihydroxyethyl fumarate, mono- or dihydroxypropyl fumarate, mono- or dihydroxyethyl itaconate and mono- or dihydroxypropyl itaconate.

In the production of the casing material according to the invention, the above mentioned copolymer generally has plasticisers and stabilisers incorporated therein. However, the copolymer may however also be used in admixture with another copolymer of vinyl chloride and vinylidene chloride.

The compound which is copolymerizable with the vinylidene chloride and the vinyl chloride is present in the film produced according to the invention in an amount of from 0.01 to 5 percent by weight of the total monomer components in the vinylidene chloride-containing copolymers. When this content falls below 0.01 percent, almost no adherence-improving effect is exhibited. On the other hand, when this content exceeds 5 percent, there is very little further improvement in the adherence, and, in addition, the possibility arises whereby the other characteristics of the vinylidene chloride series-containing film may be impaired. Furthermore, such a high content of copolymerisable compound is not economically desirable.

The proportions of vinylidene chloride to vinyl chloride, are those ordinarily used in the production of casing materials, that is, from 60 to 95 parts by weight of vinylidene chloride to from 5 to 40 parts by weight of vinyl chloride.

In some cases, other monomers copolymerizable with vinylidene chloride, vinyl chloride and the aforementioned unsaturated amide, half ester or alcoholic compound can be added in such proportions that the crystallinity of the product, which is a unique feature of copolymers of vinylidene chloride and vinyl chloride, is not impaired. Examples of these monomers, which are added in proportions of from 0.1 to 7 parts by weight, are alkyl esters (from 1 to 8 carbon atoms in the alkyl group) of unsaturated acids, such as acrylic acid, methacrylic acid, itaconic acid and maleic acid, and alkyl vinyl ethers (from 1 to 8 carbon atoms in the alkyl group).

In order that the invention may be more fully understood, the following Examples are given by way of illustration only:—

In the Examples, the numerical values of "meat adherence" and "adhesive strength" set forth, were determined by the following methods:

Meat adherence—

Casings filled with a meat product were cut up into pieces each 3 cm in width. A cut was made in the outer film skin of each piece, and the film was subjected to a stripping-off force in the circumferential direction. The weight of the film thus stripped off was measured as W_1.

The intimately adhering meat was stripped off the film, which was then washed and weighed again the weight measured being denoted by W_2.

The meat adherence was defined as (W_1-W_2)/film surface area, in the unit of milligram/cm^2.

Adhesive strength—

When carrying out the above described measurement, the force used in stripping off

the surface skin film in the circumferential direction was recorded.

The adhesive strength was defined as the average value of this force over the entire circumference, in the units of gram/cm. of width.

EXAMPLE 1

80 parts by weight of vinylidene chloride, 20 parts by weight of vinyl chloride, and 1 part by weight of monobutyl maleate were polymerized by suspension polymerization to produce a ternary polymer. For the purpose of comparison, a copolymer was separately prepared from 80 parts of vinylidene chloride and 20 parts of vinyl chloride.

5 parts of dibutyl sebacate, 2 parts of butylphthalyl butylglycolate, and 2 parts of orthophenyl glycidyl ether were added to each of the two polymers thus prepared, and from the resulting material, a film was produced by the ordinary inflation method.

Each of the two kinds of films thus produced was used to form a casing which was filled with a fish meat "ham" (kneaded fish-meat sausage-like product) prepared from 70 parts by weight of solid cubes containing 80 parts of a first species of tuna (Parathunnus sibi) and 20 parts by weight of lard, and 30 parts by weight of a minced meat hash containing 60 parts by weight of a second species of tuna (black skin tuna), 10 parts by weight of starch, 20 parts by weight of water, and 25 parts by weight of table salt. Each filled casing was heat sterilised to produce a wrapped product.

The two products thus obtained were compared, whereupon it was found that the former casing according to the present invention showed a uniform and complete adherence of the meat to film of 12 mg./cm.^{2} and had an adhesive strength of 45 g./cm. of width. In contrast, the latter strength exhibited zero values for both meat adherence and adhesive strength and liquid juices were observed to be present between the casing film and the meat surface.

EXAMPLE 2

80 parts by weight of vinylidene chloride, 20 parts by weight of vinyl chloride, and 10 parts by weight of monobutyl itaconate were polymerized by suspension polymerization to produce a ternary polymer. This polymer was blended in a proportion of 5 percent with a copolymer prepared from 80 parts by weight of vinylidene chloride and 20 parts by weight of vinyl chloride, and a film was produced from the resulting mixture, in the manner described in Example 1.

Casings made of this film were filled with the same minced meat hash which was described in Example 1 and were tested. Whereas casings made from a copolymer of vinylidene chloride and vinyl chloride which did not contain a ternary polymer exhibited zero values of meat adherence and adhesive strength, the casings of this Example according to the invention showed a meat adherence of 10 mg./cm.^{2} and an adhesive strength of 35 g./cm. of width. It was easily observable that the contents of the casings of this Example uniformly and intimately adhered to the surface of the film casing.

EXAMPLE 3

82 parts by weight of vinylidene chlorides, 18 parts by weight of vinyl chloride, and 7 parts by weight of methacrylic acid amide were emulsion polymerised to form a ternary polymer. This polymer in a proportion of 10 percent was blended with a copolymer prepared from 80 parts by weight of vinylidene chloride and 20 parts by weight of vinyl chloride, and 7 parts of dibutyl sebacate and 1 part of epoxidised soybean oil were added to the mixture. A casing film was obtained from the resulting material by the ordinary inflation method. For comparison, a casing film was prepared separately by adding the same modifiers to a copolymer which did not contain a ternary polymer.

Casings of the above described two films were respectively filled with a minced hash of a liver sausage and were then heat sterilised, and tested. As a result, it was found that the casings, according to the invention showed a meat adherence of 9 mg./cm.^{2} and an adhesive strength of 25 g./cm. of width and adhered uniformly to the meat product, whereas the other casing exhibited zero values for both meat adherence and adhesive strength and clearly showed separation of liquid juices between the film and its contents.

EXAMPLE 4

77 parts by weight of vinylidene chloride, 23 parts by weight of vinyl chloride, and 2 parts of hydroxypropyl acrylate were polymerized by the suspension polymerization process to form a ternary polymer. The same modifiers as described in Example 3 were added to this polymer, and the resulting material was used to produce casing film for packaging, which had a width of 160 mm. and a thickness of 0.04 mm., by the ordinary inflation method.

Casings made of this film were filled with minched meat hash sold on the market for use in meat sausages for domestic animals and were then heat sterilised, and tested.

As a result, a meat adherence of 20 mg./cm.^{2} and an adhesive strength of 35 g./cm. of width were indicated. Furthermore, when casings thus filled were cut and suspended, there was no tendency for their contents to slip out.

In contrast, however, when casings produced in the same manner from a copolymer of vinylidene chloride and vinyl chloride, but which did not contain hydroxypropyl acrylate, were tested under the same conditions, zero values of meat adherence and adhesive strength were obtained. When these casings filled with the meat product were cut and suspended, their contents readily slipped out.

WHAT WE CLAIM IS:—

1. A casing film having good adherence with respect to kneaded meat food products, which casing film comprises a terpolymer resin prepared by the polymerization together of vinylidene chloride, vinyl chloride, and a compound copolymerizable therewith, which compound is an amide of an unsaturated monocarboxylic acid or dicarboxylic acid having at least one amide group in the molecule, a half ester of an unsaturated dicarboxylic acid having one free carboxyl group, or an unsaturated alcoholic compound having within its molecule at least one hydroxyl group, the compound polymerizable with the vinylidene chloride and the vinyl chloride being present in the casing film in an amount of from 0.01 to 5 percent by weight, based on the total monomer components in the vinylidene chloride-containing resin.

2. A casing film as claimed in claim 1, in which the terpolymer resin is prepared by the copolymerization of a monomeric mixture consisting of from 60 to 95 percent by weight of vinylidene chloride, from 5 to 40 percent by weight of vinyl chloride, with the compound copolymerizable therewith defined in claim 1.

3. A casing film as claimed in claim 1, in which the resin is prepared by the copolymerization of a monomeric mixture consisting of from 60 to 95 percent by weight of vinylidene chloride, from 4.9 to 39.9 percent by weight of vinyl chloride, and from 0.1 to 7 percent by weight of a further monomer copolymerizable with the vinylidene chloride and vinyl chloride, with the compound copolymerizable with the vinylidene chloride and the vinyl chloride defined in claim 1.

4. A casing film as claimed in claim 3, in which the monomer present in an amount of from 0.1 to 7 percent by weight of the said monomeric mixture is an alkyl ester of an unsaturated carboxylic acid having from 1 to 8 carbon atoms in its alkyl group, or an alkyl vinyl ether having from 1 to 8 carbon atoms in its alkyl group.

5. A casing film as claimed in claim 4 wherein the alkyl ester is an ester of acrylic acid, methacrylic acid or itaconic acid.

6. A casing film as claimed in any one of claims 1 to 5 in which the compound copolymerisable with vinyl chloride and vinylidene chloride is a monoamide or diamide of acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, or aconitic acid, or a monoester of maleic acid, fumaric acid, itaconic acid or aconitic acid.

7. A casing film as claimed in any one of claims 1 to 5 in which the unsaturated alcoholic compound is allyl alcohol, methallyl alcohol, or a hydroxyalkyl ester, having from 2 to 6 carbon atoms in its alkyl group, of acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, or aconitic acid.

8. A casing film as claimed in any one of claims 1 to 7 in which the terpolymer is used in admixture with a copolymer of vinyl chloride and vinylidene chloride.

9. A process for producing a film material for encasing kneaded meat food products, in which a copolymer resin is prepared by copolymerizing vinylidene chloride, vinyl chloride, and a compound copolymerizable therewith, which compound is an amide of an unsaturated monocarboxylic or dicarboxylic acid having at least one amide group in the molecule, a half ester of an unsaturated dicarboxylic acid having one free carboxyl group, or an unsaturated alcohol having within its molecule at least one hydroxyl group, the compound polymerizable with the vinylidene chloride and vinyl chloride being present in an amount of from 0.01 to 5 percent by weight based on the total monomer components in the vinylidene chloride-containing resin, and forming the film material from the copolymer resin thus prepared.

10. A process as claimed in claim 9, in which the copolymer resin is prepared by the copolymerization of a monomeric mixture consisting of from 60 to 95 percent by weight of vinylidene chloride and from 5 to 40 percent by weight of vinyl chloride, with the compound copolymerizable therewith defined in claim 1.

11. A process as claimed in claim 9, in which the copolymer resin is prepared by the copolymerization of a monomeric mixture consisting of from 60 to 95 percent by weight of vinylidene chloride, from 4.9 to 39.9 percent by weight of vinyl chloride, and from 0.1 to 7 percent by weight of a further monomer copolymerizable with the vinylidene chloride and vinyl chloride with the compound copolymerizable with the vinyl chloride and vinylidene chloride defined in claim 1.

12. A process as claimed in claim 11, in which the monomer present in an amount of from 0.1 to 7 percent by weight of said monomeric mixture is an alkyl ester of an unsaturated carboxylic acid having from 1 to 8 carbon atoms in its alkyl group or an alkyl vinyl ether having from 1 to 8 carbon atoms in its alkyl group.

13. A process as claimed in claim 12 in which the alkyl ester is an ester of acrylic acid, methacrylic acid or itaconic acid.

14. A process as claimed in any one of claims 9 to 13, inclusive, in which the compound copolymerisable with vinyl chloride and vinylidene chloride is a monoamide or diamide of acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, aconitic acid, or a monoester of maleic acid, fumaric acid, itaconic acid, or aconitic acid.

15. A process as claimed in any one of claims 9 to 13, inclusive, in which the unsaturated alcoholic compound is allyl alcohol, methallyl alcohol, or a hydroxyalkyl ester, having from 2 to 6 carbon atoms in its alkyl group, of acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, or aconitic acid.

16. A process as claimed in any one of claims 9 to 15 in which the terpolymer is used in admixture with a copolymer of vinyl chloride and vinylidene chloride.

17. A process for providing a film material for encasing kneaded meat products as claimed in claim 9, substantially as herein described with reference to the Examples.

18. A casing film material when produced by the process claimed in any one of claims 9 to 17.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1969.
Published by the Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.